

CLAIMS

1. A self setting calcium phosphate cement comprising:-
 - (i) a powdered component, said powdered component having an average particle size d_{50} of less than 15 μm , and
 - (ii) a calcium phosphate based powder, said powder having an average particle size d_{50} greater than that of the powdered component, said powdered component and said calcium phosphate based powder being suspended in water containing a dissolved zeta potential increasing additive in sufficient quantity to increase the zeta potential of the suspended particles to at least 30 mV, and wherein the zeta potential increasing additive is chosen to be compatible with the setting pH of the same calcium phosphate cement without the zeta potential increasing additive.
2. A cement as claimed in claim 1, wherein the d_{50} of the calcium phosphate based powder is from 1.5 to 10 times greater than the d_{50} of the powdered component.
3. A cement as claimed in claims 1 or 2, wherein the zeta potential increasing additive is an oligocarboxylic acid compound.
4. A cement as claimed in claim 3, wherein the oligocarboxylic acid compound has two or three carboxyl groups.
5. A cement as claimed in claims 3 or 4 wherein the oligocarboxylic acid compound has one or more hydroxyl groups.

6. A cement as claimed in any one of claims 3 to 5 wherein the oligocarboxylic acid compound is selected from citric acid, tartaric acid and malic acid.
7. A cement as claimed in any one of claims 3 to 5, wherein the calcium phosphate based cement sets at an approximately neutral pH, and the oligocarboxylic acid compound is a salt of the carboxylic acid selected from a group I or group II metal salt an ammonium salt or a mixed salt.
8. A cement as claimed in claim 7 wherein said salt is trisodium citrate, disodium malate or disodium tartrate.
9. A cement as claimed in any preceding claim, wherein the zeta potential increasing additive is in sufficient quantity to increase the zeta potential of the calcium phosphate particles to at least -40 and preferably at least -50 mV.
10. A cement as claimed in any preceding claim, wherein the zeta potential increasing additive is present in an amount of from 0.01 to 2 Mol per litre of water, more preferably 0.1 to 1 Mol per litre and most preferably 0.2 to 1 M per litre.
11. A cement as claimed in any preceding claim, wherein the powdered component has a d_{50} of no more than $10\text{ }\mu\text{m}$, and preferably no more than $5\text{ }\mu\text{m}$.
12. A cement as claimed in any preceding claim, wherein the powdered component is selected from calcium phosphate, dicalcium phosphate anhydrous, dicalcium phosphate dihydrate, α -tricalcium phosphate, β -tricalcium

phosphate, tetracalcium phosphate, hydroxyapatite, octacalcium phosphate or substituted forms thereof.

13. A cement as claimed in any one of claims 1 to 11, wherein the powdered component is a carbonate, silicate, nitrate, oxide or sulphate and/or a salt of calcium, zirconium, aluminium, titanium or silicon, or mixtures thereof.

14. A cement as claimed in any preceding claim, wherein the calcium phosphate based material has a d_{50} of at least 3 μm .

15. A cement as claimed in any preceding claim, wherein the calcium phosphate based material is tetracalcium phosphate, α - or β -tricalcium phosphate, hydroxyapatite, monocalcium phosphate monohydrate, monocalcium phosphate anhydrous or mixtures thereof.

16. A cement as claimed in any preceding claim, wherein the calcium phosphate based material is mechanically activated.

17. A cement as claimed in any preceding claim, wherein the volume ratio of the calcium phosphate based powder to the powdered component is in the range of from 50:50 to 95:5.

18. A cement as claimed in any preceding claim, wherein the powdered component constitutes no more than 40% by volume of the calcium phosphate based powder.

19. A cement as claimed in claim 18, wherein the powdered component constitutes no more than 30% by volume of the calcium phosphate based powder
20. A cement as claimed in claim 19, wherein the powdered component constitutes from 10 to 25% by volume of the calcium phosphate based powder.
21. A shelf-stable acidic setting cement powder comprising :-
- (i) a calcium phosphate based powder, and
 - (ii) a powdered compound which, upon addition of water to form a cement paste, retards the cement setting reaction or increases the zeta potential of the resultant suspended particles to at least -30 mV.
22. A cement powder as claimed in claim 21, wherein said calcium phosphate based powder comprises β -TCP or α -TCP.
23. A cement powder as claimed in claim 22, additionally comprising at least one of monocalcium phosphate anhydrous, monocalcium monohydrate, dicalcium phosphate anhydrous, dicalcium phosphate dihydrate, α -tricalcium phosphate, β -tricalcium phosphate, tetracalcium phosphate, hydroxyapatite, octacalcium phosphate or substituted forms thereof.
24. A cement powder as claimed in any one of claims 21 to 23, wherein the powdered component is selected from an oligocarboxylic acid compound and a pyrophosphate salt.
25. A cement powder as claimed in claim 24, wherein the oligocarboxylic acid compound has two or three carboxyl groups.

26. A cement powder as claimed in claim 24 or 25, wherein the oligocarboxylic acid compound is selected from citric acid, tartaric acid and malic acid.
27. A cement powder as claimed in any one of claims 24 to 26, wherein the oligocarboxylic acid compound is salt of the carboxylic acid selected from a group I or group II metal salt an ammonium salt or a mixed salt.
28. A cement powder as claimed in any one of claims 21 to 27, wherein the powdered component is present in the range from 0.1 to 20mol% of the calcium phosphate based powder.
29. A cement powder comprising:-
- (i) a powdered component, said powdered component having an average particle size d_{50} of less than 15 μm , and
 - (ii) a calcium phosphate based powder, said powder having an average particle size d_{50} greater than that of the powdered component.
30. A cement powder as claimed in claim 29, additionally comprising a powdered compound which, upon addition of water to form a cement paste, retards the cement setting reaction or is a zeta potential increasing additive, said cement powder having an extended shelf life.